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STUDIES ON THE CONVERSION OF PENTABORANE(9) TO DECABORANE(14). --ETC(U)
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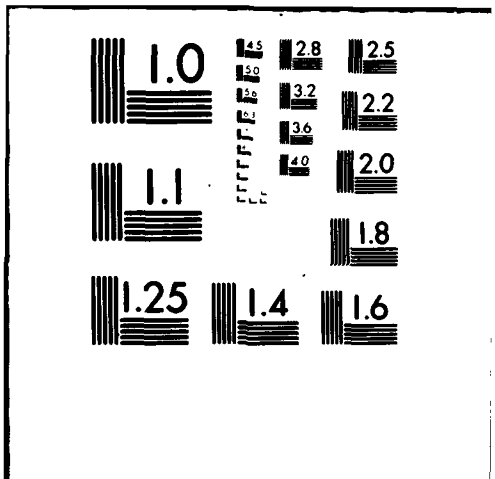

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AD A092995

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 15611.6-C
2. GOVT ACCESSION NO.: AD-A092 995
3. RECIPIENT'S CATALOG NUMBER:
4. TITLE (and Subtitle): Studies on the Conversion of Pentaborane(9) to Decaborane(14), Part III.
5. TYPE OF REPORT & PERIOD COVERED: Technical
6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): Sheldon G. Shore, Mark A. Toft
8. CONTRACT OR GRANT NUMBER(s): DAAG29-78-G-0112
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Ohio State University, Columbus, OH 43210
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, Post Office Box 12211, Research Triangle Park, NC 27709
12. REPORT DATE: Dec 80
13. NUMBER OF PAGES: 5
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

LEVEL

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DTIC ELECTE DEC 12 1980 S D C

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

boranes
chemical reactions
reagents
laboratory techniques
chemical reactors

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report supercedes and makes obsolete two earlier technical reports (Parts I and II) submitted to ARO entitled: "Studies on the Conversion of Pentaborane(9) to Decaborane(14)". We now have a simple method for producing in the laboratory good quality $B_{10}H_{14}$ from B_5H_9 in yields of 42-45%. Additionally we have been able to replace the costly reagents KH, BBr_3 and $N(n-C_4H_9)_4Br$ with the much cheaper reagents NaH, BCl_3, $N(CH_3)_4Cl$. We believe that this procedure is ready for scale up tests in ½ to 1 pound quantities in a pilot plant reactor. Given below is a detailed description of our laboratory procedure for preparing $B_{10}H_{14}$ in 1 gram quantities.

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267200 80 12 12 125

Technical Report

STUDIES ON THE CONVERSION OF PENTABORANE(9) TO DECABORANE(14)

PART III

ARO PROPOSAL NUMBER: 08999-55-00

TITLE OF PROPOSAL: Studies on the Syntheses of Boron Hydride Systems

CONTRACT OR GRANT NUMBER: DAAG29-78-G-0112

NAME OF INSTITUTION: The Ohio State University

PRINCIPAL INVESTIGATOR: Sheldon G. Shore, Professor of Chemistry

REPORT PREPARED BY: Professor Sheldon G. Shore

Mark A. Toft

INTRODUCTION

This report supercedes and makes obsolete two earlier technical reports (Parts I and II) submitted to ARO entitled: "Studies on the Conversion of Pentaborane(9) to Decaborane(14)". We now have a simple method for producing in the laboratory good quality $B_{10}H_{14}$ from B_5H_9 in yields of 42-45%. Additionally we have been able to replace the costly reagents KH, BBr_3 and $[N(\underline{n}\text{-}C_4H_9)_4]Br$ with the much cheaper reagents NaH, BCl_3, $[N(CH_3)_4]Cl$. We believe that this procedure is ready for scale-up tests in ½ to 1 pound quantities in a pilot plant reactor.

Given below is a detailed description of our laboratory procedure for preparing $B_{10}H_{14}$ in 1 gram quantities. It should be recognized that the laboratory method employs glass reactors and vacuum line techniques which are convenient for relatively small scale preparations. Some of the procedures employed in the laboratory method would be obviated in a scale-up procedure in which a metal reactor and metal piping would be employed. Thus, for example, while we condense B_5H_9 into a small glass reactor under vacuum at -196°, in a large scale procedure liquid B_5H_9 would be forced from its storage cylinder into the metal reqctor by N_2 gas. In the stage where we maintain the mixture of BCl_3 and $[N(CH_3)_4][B_9H_{14}]$ at 11°, this is done to avoid excessive pressure in the glass reactor. With the metal reactor, room temperature would be permissible. Although vacuum sublimation is used to isolate $B_{10}H_{14}$ in the laboratory method, in the scaled-up procedure a stream of N_2 gas could be passed over the subliming $B_{10}H_{14}$ at 110° and a water-cooled collector would be sufficient to trap the $B_{10}H_{14}$.

A CONVENIENT LABORATORY PREPARATION OF $B_{10}H_{14}$ FROM B_5H_9

This procedure consists of three distinct steps or stages.

1. Conversion of B_5H_9 to $[N(CH_3)_4]B_9H_{14}$ by reacting a 2:1 molar ratio of B_5H_9 with NaH in THF in the presence of $[N(CH_3)_4]Cl$ at room temperature.

2. After completion of step 1, THF is removed from the system and BCl_3 is added to the solid $[N(CH_3)_4][B_9H_{14}]$ and allowed to react at 11°.

3. After completion of step 2, $B_{10}H_{14}$ is sublimed at 110° from the solid reaction mixture.

Details of each of these steps follow.

1. 513 mg NaH (21.4 millimoles), 2.30 g $[(CH_3)_4N][Cl]$ (22 millimoles), and a magnetic stirring bar (1½" long) are placed in a 500 ml roundbottom flask in a dry box using N_2 atmosphere. The 500 ml flask is single neck with a 15 mm solv-seal joint glassblown in place of the normal neck opening. A reaction vessel to vacuum line stopcock adapter is attached to the 500 ml flask via this 15 mm solv-seal joint. The adapter is comprised of a 0 to 4 mm bore Kontes teflon stopcock to which is attached on one side a 15 mm solv-seal joint and on the other side a standard taper 14/35 outer joint.

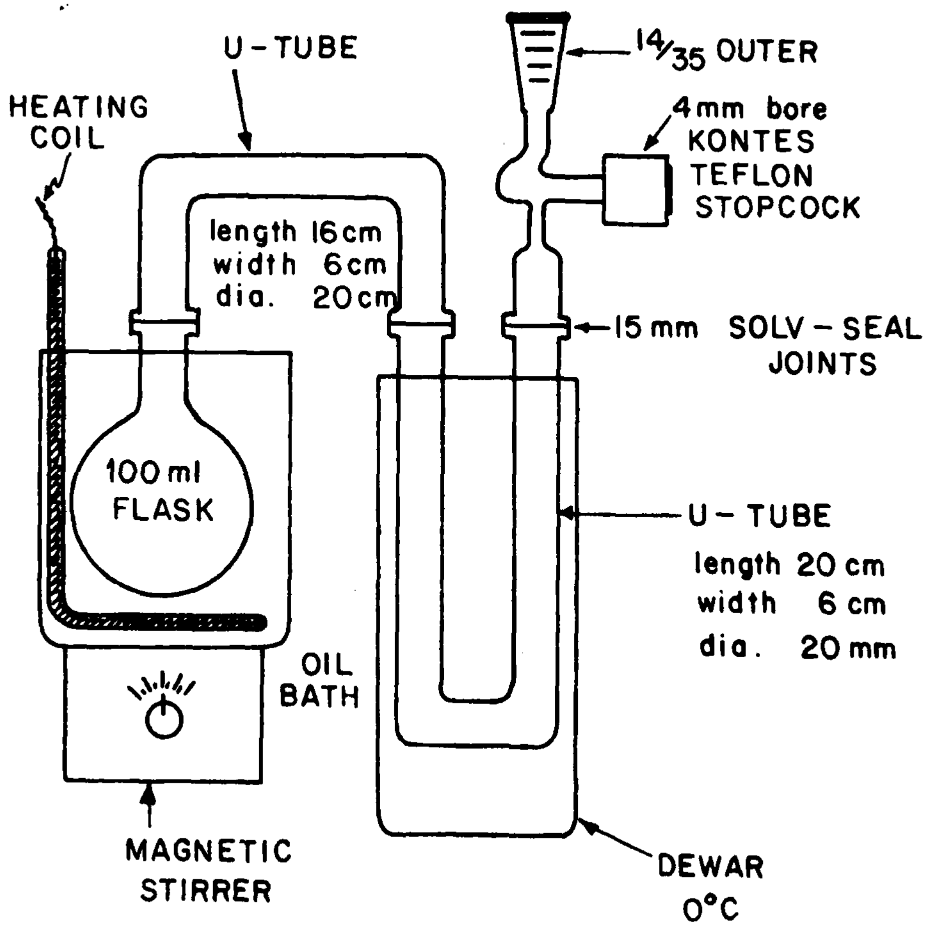
The reaction vessel (500 ml flask and stopcock adapter) is then removed from the dry box and attached to an inlet port of a standard vacuum line. The reaction vessel is evacuated of dry box N_2 and 20 ml of dry THF is condensed into the reaction vessel which is maintained at -78°C using a dry ice/isopropanol slush. The dry ice/isopropanol slush is then replaced with a liquid N_2 dewar and 4.10 ml B_5H_9 (42.8 mmoles), the volume measured at 0°C where the density of B_5H_9 is .66 g/m is then condensed into the reaction vessel. The reaction mixture is then warmed to room temperature (26-27°C) and is stirred vigorously for 12 hours. Immediate gas evolution is present and continues for several minutes.

The solution gradually changes from a clear slurry to light yellow. After 12 hours the reaction vessel is cooled to -196°C and the H_2 produced is measured via a calibrated toepler system. 22 millimoles of H_2 is obtained and this corresponds to initial deprotonation of one equivalent of B_5H_9 with one equivalent of NaH. The reaction vessel is then warmed to 0°C while the solvent is removed under vacuum by pumping through a U-trap maintained at -78°C and a U-trap maintained at -196°C. Total solvent removal takes 3 hours, with the reaction vessel warmed to room temperature after 2 hours. The solid remaining is very light yellow and consists of $[(CH_3)_4N][B_9H_{14}]$ and NaCl. ^{11}B NMR at 32.1 MHz shows the only boron containing species to be $B_9H_{14}^-$.

2. The $[(CH_3)_4N][B_9H_{14}]$ from step 1 is then scraped from the 500 ml reaction vessel and transferred to a similarly equipped 100 ml reaction vessel in the dry box. The stir bar is also transferred. Only a few, <10 mg are lost in the transfer. NOTE: The solid transferred also contains NaCl.

The 100 ml reaction vessel is removed from the dry box, placed on an inlet port of the vacuum line and evacuated of dry box N_2. 22.0 mmoles of BCl_3 (freed from HCl) measured by gas volume at 26°C are condensed into the reaction vessel maintained at -196°C. The reaction vessel is then warmed to 11°C (H_2O and small quantity of ice) and stirred.

3. After 4 hours the reaction mixture is cooled to -196°C and 11 mmoles H_2 is removed using the aforementioned toepler system. The reaction vessel is then warmed to room temperature and traces of volatile materials are removed by pumping for a few minutes. The reaction vessel is then removed to the dry box where it is attached to a special "sublimator" for removal of $B_{10}H_{14}$. The "sublimator" system used is diagrammed below.



The U-tube is maintained at 0°C while the reaction vessel is slowly warmed to 110°C. The entire system is under dynamic vacuum. Decaborane collects slowly in the bridge and finally in the U-tube over a 2-hour period. Initially the $B_{10}H_{14}$ obtained is white but eventually is tinted light yellow by reaction by-products blown through the system due to dynamic vacuum. The amount of inpurity is however, quite small (a few milligrams). The initial mass of $B_{10}H_{14}$ obtained is 1.18 g or 45.2% based on B_5H_9. This is slightly reduced upon recrystallization which yields much purer $B_{10}H_{14}$ in a 1.10 g quantity or 42.1% yield based on B_5H_9 used. The ^{11}B NMR of the $B_{10}H_{14}$ shows it to be quite pure.